

Poly(*p*-phenylene terephthalamide) Film as a Matrix Film for Electrochromic V₂O₅ and the Improvement of the ECD Properties

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Among inorganic ECD materials, vanadium pentoxide (V₂O₅) films have attracted attention for use in multicolored ECDs [1]. The V₂O₅ films readily deteriorate and exhibit no electrochromism when they are subject to over-oxidation or over-reduction. Moreover, without the over-oxidation or over-reduction, the films peel off the electrode substrates after about 1500 color change cycles [2]. To enhance the durability, we have used an aramid resin, poly(*p*-phenylene terephthalamide) (PPTA), as a matrix film and prepared the PPTA-V₂O₅ composite film.

The PPTA film was obtained on an indium-tin oxide (ITO) [3]. On the ITO electrode and the PPTA film-coated ITO electrode, V₂O₅ was electrodeposited from aqueous electrolyte solution containing VOSO₄ until the passed charge reached 2.0 C cm⁻². The cyclic voltammograms of the obtained the V₂O₅ and PPTA-V₂O₅ composite films were measured, and both voltammograms were almost the same shape. Significantly, however, the absorption spectra were different from each other (Figs. 1 and 2). The absorbance ranging from 600 to 900 nm changes more remarkably in the PPTA-V₂O₅ film than in the V₂O₅ film. The PPTA-V₂O₅ film exhibits higher contrast ratio.

In the reduced state of the PPTA-V₂O₅ film (Fig. 2 (a)), the absorbance peak is evident at about 800 nm, and the film becomes green. On the other hand, the V₂O₅ film is bluish green at -0.6 V. The XPS signal peak of V(2p) of the PPTA-V₂O₅ film was 1.5 eV lower than that of the V₂O₅ film, implying that the lower valency of vanadium, V(III) as well as V(IV), exists in the PPTA-V₂O₅ film. The PPTA-V₂O₅ film showed no blue color due to the relatively small amount of V(V), compared with V(III) and V(IV). This is probably due to the simultaneous presence of carbonyl and amino groups on the polymeric backbone whose lone pair electrons are available to coordinate with V(V). In addition, the electronic coordination of PPTA prevented V₂O₅ from degrading and from peeling off the electrode substrate during the repetitive color changes under anodic and cathodic polarizations. No color change took place after 200 repetitions for the V₂O₅ film, while a color change was obtained even after 5000 repetition for the PPTA-V₂O₅ film.

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[1] C. G. Granqvist, Handbook of Inorganic Electrochromic Materials, Elsevier, Amsterdam, 1995.

[2] S. Yamasaki *et al.*, Hyomen Gijutu, **49** (1998) 990.

[3] K. Koga *et al.*, Polym. J. **21** (1989) 733.

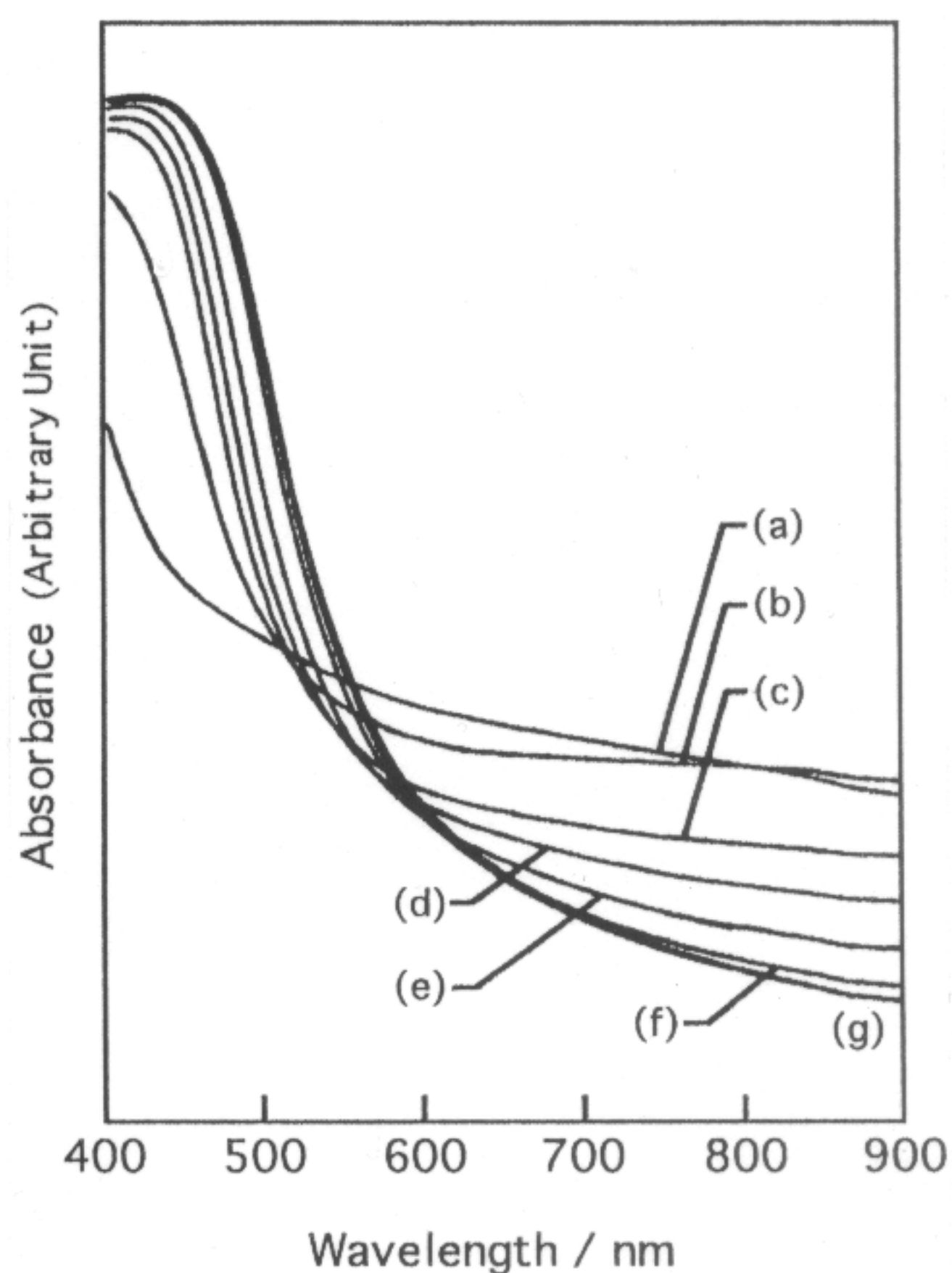


Fig. 1 Optical absorption spectrum of the V₂O₅ film *in situ* at various electrode potentials: (a) -0.6; (b) -0.4; (c) -0.2; (d) 0; (e) +0.2; (f) +0.4; (g) +0.8V vs. Ag⁺/Ag.

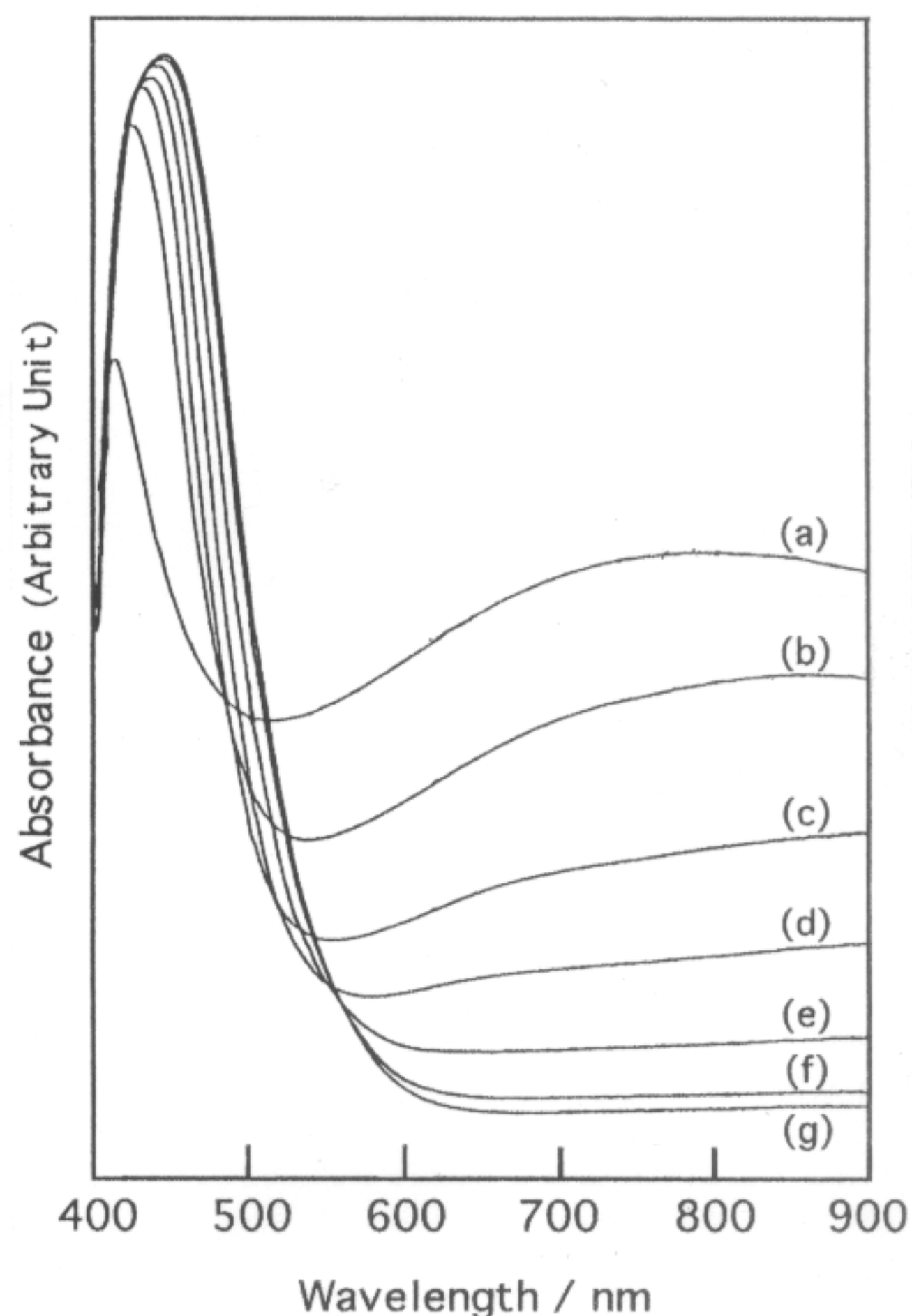


Fig. 2 Optical absorption spectrum of the PPTA-V₂O₅ film *in situ* at various electrode potentials: (a) -0.6; (b) -0.4; (c) -0.2; (d) 0; (e) +0.2; (f) +0.4; (g) +0.8V vs. Ag⁺/Ag.